Novel Thermal Reaction of Fischer Carbene Complexes with Imines:

Synthesis of β -Methoxy Allylic Amine Derivatives

Kenichiro Sangu, Hirotaka Kagoshima, Kohei Fuchibe, and Takahiko Akiyama*

Department of Chemistry, Faculty of Science, Gakushuin University,

1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

takahiko.akiyama@gakushuin.ac.jp

Supporting Information

General: All the materials were purified by distillation or recrystallization. THF and diethyl ether were distilled from sodium benzophenone ketyl before use. Dichloromethane was distilled from calcium hydride before use. All of the solvents other than THF, diethyl ether, and dichloromethane were distilled and stored over molecular sieves 3A. Preparative thin layer chromatography (preparative TLC) was conducted on silica gel (Wakogel B-5F, Wako Pure Chemical Industries). All the reactions were carried out under a nitrogen atmosphere.

NMR spectra were recorded on Unity Inova-400 instrument (Varian Japan Ltd., 400 MHz for ^1H , 100 MHz for ^{13}C) using CDCl_3 as a solvent. Chemical shifts (δ) for ^1H were referenced to tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. Chemical shifts (δ) for ^{13}C were referenced to a solvent signal (CDCl_3 , $\delta = 77.00$ ppm). IR spectra were recorded on FTIR-8600PC instrument (Shimadzu Co.) using CHCl_3 as a solvent. Elemental analysis (EA) was carried out on EA1110 instrument (Amco Inc.).

Preparation of Materials: Carbene complexes and imines were prepared according to the literatures. For preparation of carbene complexes, see; Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954. For preparation of aromatic imines, see; Ishimaru, K.; Watanabe, K.; Yamamoto, Y.; Akiba, K. *Synlett* **1994**, 495. For preparation of aliphatic imines; Chemla, F; Hebbe, V; Normant, J. –F. *Synthesis* **2000**, 75.

Spectra Data of Products: *N*-Tosyl-2-methoxy-1-phenylprop-2-en-1-amine **5a**: ^1H NMR δ 2.40 (s, 3H), 3.33 (s, 3H), 3.92 (d, $J = 2.7$ Hz, 1H), 4.06 (d, $J = 2.7$ Hz, 1H), 4.98 (d, $J = 8.8$ Hz, 1H), 5.27 (d, $J = 8.8$ Hz, 1H), 7.19-7.28 (m, 7H), 7.67 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 21.47, 54.98, 60.28, 84.48, 126.77, 127.27, 127.65, 128.31, 129.19, 137.57, 138.44, 143.09, 159.26; IR ν 3379, 3030, 1632, 1335, 1161 cm^{-1} ; EA Found: C, 64.56%; H, 6.03%; N, 4.68%; S, 10.11%. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3\text{S}$: C, 64.33%; H, 6.03%; N, 4.41%; S, 10.10%.

N-Tosyl-2-methoxy-1-(1-naphthyl)prop-2-en-1-amine **5b**: ^1H NMR δ 2.37 (s, 3H), 3.34 (s, 3H), 3.99 (d, $J = 2.9$ Hz, 1H), 4.12 (d, $J = 2.9$ Hz, 1H), 5.23 (d, $J = 8.1$ Hz, 1H), 5.75 (d, $J = 8.1$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 7.7$ Hz, 1H), 7.39 (d, $J = 6.8$ Hz, 1H), 7.44-7.51 (m, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.79-7.83 (m, 1H), 8.11 (d, $J = 7.1$ Hz, 1H); ^{13}C NMR δ 21.44, 55.02, 57.05, 84.59, 123.33, 125.00, 125.20, 125.67, 126.46, 127.39, 128.66, 128.77, 129.05, 130.80, 133.81, 134.03, 137.40, 143.02, 159.99; IR ν 3381, 1599, 1335, 1159, 667 cm^{-1} ; EA Found: C, 68.61%; H, 5.60%; N, 3.62%; S, 9.00%. Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_3\text{S}$: C, 68.64%; H, 5.76%; N, 3.81%; S, 8.73%.

N-Tosyl-1-(*p*-chlorophenyl)-2-methoxyprop-2-en-1-amine **5c**: ^1H NMR δ 2.41 (s, 3H), 3.33 (s, 3H), 3.92 (d, $J = 2.9$ Hz, 1H), 4.03 (d, $J = 2.9$ Hz, 1H), 4.94 (d, $J = 8.5$ Hz, 1H), 5.34 (d, $J = 8.5$ Hz, 1H), 7.18-7.25 (m, 6H), 7.65 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR δ 21.48, 55.09, 59.81, 84.74, 127.26, 128.29, 128.42, 129.27, 133.57, 137.03, 137.46, 143.31, 158.95; IR ν 3381, 3030, 1634, 1491, 1337, 1161 cm^{-1} ; EA Found: C, 58.09%; H, 5.20%; N, 3.85%; S, 9.30%. Calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_3\text{S}$: C, 58.03%; H, 5.16%; N, 3.98%; S, 9.11%.

N-Tosyl-1-(*p*-cyanophenyl)-2-methoxyprop-2-en-1-amine **5d**: ^1H NMR δ 2.42 (s, 3H), 3.35 (s, 3H), 3.95 (d, $J = 3.1$ Hz, 1H), 4.03 (d, $J = 3.1$ Hz, 1H), 5.00 (d, $J = 8.7$ Hz, 1H), 5.45 (d, $J = 8.7$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.54 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 21.51, 55.22, 60.08, 85.36, 111.56, 118.55, 127.21, 127.68, 129.39, 132.09, 137.27,

143.59, 143.83, 158.19; IR ν 3381, 3028, 2232, 1636, 1339, 1161 cm^{-1} ; EA Found: C, 63.20%; H, 5.14%; N, 8.49%; S, 9.50%. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: C, 63.13%; H, 5.30%; N, 8.18%; S, 9.36%.

N-Tosyl-2-methoxy-1-(*p*-tolyl)prop-2-en-1-amine **5e**: ^1H NMR δ 2.30 (s, 3H), 2.41(s, 3H), 3.32(s, 3H), 3.91 (d, J = 2.8 Hz, 1H), 4.06 (d, J = 2.8 Hz, 1H), 4.94 (d, J = 8.8 Hz, 1H), 5.18 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.3 Hz, 2H), 7.67 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 21.02, 21.48, 55.00, 60.08, 84.32, 126.68, 127.31 129.03, 129.19, 135.53, 137.44, 137.67, 143.05, 159.49; IR ν 3379, 3028, 1632, 1335, 1161 cm^{-1} ; EA Found: C, 65.15%; H, 6.54%; N, 4.14%; S, 9.64%. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3\text{S}$: C, 65.23%; H, 6.39%; N, 4.23%; S, 9.68%.

N-Tosyl-2-methoxyhept-1-en-3-amine **5f**: ^1H NMR δ 0.84 (t, J = 7.0 Hz, 3H), 1.14-1.30 (m, 4H), 1.49-1.57 (m, 2H), 2.40 (s, 3H), 3.22 (s, 3H), 3.65 (d, J = 2.7 Hz, 1H), 3.75 (dt, J = 2.6, 9.7 Hz, 1H), 3.78 (d, J = 2.7 Hz, 1H), 4.82 (d, J = 8.9 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.66 (d, J = 7.9 Hz, 2H); ^{13}C NMR δ 13.86, 22.14, 27.85, 33.95, 54.59, 57.53, 82.96, 127.26, 129.10, 138.07, 142.87, 159.61.

N-Tosyl-2-methoxy-4-methylpent-1-en-3-amine **5g**: ^1H NMR δ 0.81 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.76 (octet, J = 6.8 Hz, 1H), 2.40 (s, 3H), 3.21 (s, 3H), 3.44 (dd, J = 8.1, 10.0 Hz, 1H), 3.65 (d, J = 2.6 Hz, 1H), 3.71 (d, J = 2.6 Hz, 1H), 4.84 (d, J = 10.0 Hz, 1H), 7.25 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 19.01, 19.33, 21.46, 31.52, 54.50, 63.38, 83.86, 127.27, 129.05, 138.06, 142.82, 158.67; IR ν 3369, 2964, 1628, 1331, 1161 cm^{-1} ; EA Found: C, 59.31%; H, 7.12%; N, 4.80%; S, 11.08%. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_3\text{S}$: C, 59.34%; H, 7.47%; N, 4.94%; S, 11.32%.

N-Tosyl-1-cyclohexyl -2-methoxyprop-2-en-1-amine **5h**: ^1H NMR δ 0.82-0.98 (m, 2H), 1.05-1.22 (m, 3H), 1.36-1.77 (m, 5H), 1.96 (d, J = 13.0 Hz, 1H), 2.40(s, 3H), 3.20(s, 3H), 3.48 (dd, J = 8.6, 9.8 Hz, 1H), 3.64 (d, J = 2.7 Hz, 1H), 3.68 (d, J = 2.7 Hz, 1H), 4.82 (d, J = 9.8 Hz, 1H), 7.23 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 21.47, 25.87, 25.92, 26.22, 29.49, 29.69, 40.48, 54.52, 62.61, 83.98, 127.27, 129.04, 138.16, 142.78, 158.32; IR ν 3369, 2932, 1450, 1333, 1161 cm^{-1} ; EA Found: C, 63.19%; H, 7.94%; N, 4.36%; S, 9.52%. Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{S}$: C, 63.13%; H, 7.79%; N, 4.33%; S, 9.91%.

N-Tosyl-2-methoxy-1-phenylhex-2-en-1-amine **12** (Data for diastereomeric mixture are shown. Diastereomer ratio was determined by the integrals of the olefinic triplet, 58:42. Geometry of the carbon-carbon double bond was not determined): ^1H NMR δ 0.83 (t, $J = 5.7$ Hz, 3H), 1.18-1.29 (m, 2H), 1.80-1.99 (m, 2H), 2.39 (s, 3H*0.42), 2.40 (s, 3H*0.58), 3.24 (s, 3H*0.58), 3.37 (s, 3H*0.42), 4.31 (t, $J = 7.3$ Hz, 1H*0.58), 4.62 (t, $J = 7.3$ Hz, 1H*0.42), 4.94 (d, $J = 7.8$ Hz, 1H*0.42), 5.18 (d, $J = 7.8$ Hz, 1H*0.42), 5.38 (d, $J = 9.6$ Hz, 1H*0.58), 5.51 (d, $J = 9.6$ Hz, 1H*0.58), 7.19-7.35 (m, 7H), 7.67 (t, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 13.71, 13.74, 21.42, 22.68, 23.51, 27.24, 28.22, 54.14, 54.88, 59.60, 59.74, 100.07, 114.58, 126.75, 126.99, 127.12, 127.20, 127.43, 127.52, 128.30, 129.11, 129.29, 137.66, 137.85, 138.75, 138.80, 142.96, 143.10, 150.86, 152.67; IR $\tilde{\nu}$ 3364, 2961, 1335, 1215, 1159, 716 cm^{-1} ; EA Found: C, 66.76%; H, 7.07%; N, 3.92%; S, 8.67%. Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_3\text{S}$: C, 66.82%; H, 7.01%; N, 3.90%; S, 8.92%.